

CHARGED SURFACE MODIFYING MACROMOLECULES IN POLYMER ELECTROLYTE MEMBRANE

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Abstrak. Charged surface modifying macromolecule (cSMM) end capped with sulfonic group was prepared and blended into sulfonated poly (ether ether ketone) (SPEEK). The modified membrane was characterized for polymer electrolyte membrane application; *i.e.* a SPEEK/cSMM blend membrane was compared to a SPEEK membrane and a Nafion 112 membrane for the thermal and mechanical stability, hydrophilicity and water uptake. Thermal and mechanical stability of the blend membrane were slightly reduced from that of the SPEEK membrane but still higher than that of the Nafion 112 membrane. The blend membrane showed an increase in hydrophilicity and water uptake as compared to the pristine membrane. The addition of cSMM has enabled the water uptake to be increased which is crucial to enhance the proton conductivity that of SPEEK. This study found that cSMM is a good candidate as an additive for SPEEK in improving its function as polymer electrolyte membrane.

Keywords: Direct methanol fuel cell; proton exchange membrane; sulfonated poly (ether ether ketone), charged surface modifying macromolecule

Abstract. Pengubah permukaan molekul makro bercas (cSMM) yang dilengkapi dengan kumpulan sulfurik di hujungnya telah disediakan dan dicampurkan ke dalam poly (ether ether ketone) bersulfonat (SPEEK). Membran yang dicampurkan itu telah dibuat pengelasan untuk kegunaan membran polimer elektrolit, di mana campuran SPEEK/cSMM telah dibandingkan dengan SPEEK dan Nafion 112 terhadap kestabilan suhu, kestabilan mekanikal, kecenderungan terhadap air dan penyerapan air. Kestabilan suhu dan kestabilan mekanikal membran campuran berkurangan sedikit dari SPEEK asal tetapi masih tinggi berbanding membran Nafion 112. Membran campuran menunjukkan peningkatan dalam kecenderungan terhadap air dan ia juga menunjukkan peningkatan dalam penyerapan air berbanding membran asal. Penambahan cSMM telah membolehkan penyerapan air bertambah, yang merupakan faktor penting untuk meningkatkan pengaliran proton dalam SPEEK. Pembelajaran ini mendapati cSMM adalah satu calon yang baik sebagai bahan penambah ke dalam SPEEK untuk meningkatkan fungsinya sebagai membran polimer elektolit.

Kata kunci: Bahan api metanol terus; membran pertukaran proton; sulfana poli (eter eter kiton); permukaan bercas mengubah suai molekul makro

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1.0 INTRODUCTION

The heart of direct methanol fuel cell (DMFC) is the proton exchange membrane (PEM) which separates catalyzed cathode and anode electrodes. The conventional PEM material used in DMFC is Nafion[®]. However, it has three major disadvantages of high cost, loss of conductivity at temperatures above 80 °C and high methanol crossover that has limited its applications. The high methanol crossover from anode to cathode is a major problem since it wastes fuel and causes performances losses at the cathode due to the consumption of oxygen and leads to poisoning of the catalyst.

Various efforts were made along different directions aimed to develop alternative replacement of Nafion which are more economical, have higher operating temperatures, as well as higher proton conductivity and low methanol permeability. Among them, particularly poly(ether ether ketone) (PEEK) has been extensively studied by many researchers for instance on cross-linking [1], composite membranes with inorganic materials [2, 3], blend membranes with other polymers [4] and surface modification [5, 6] such as plasma treatment and grafting reaction, surface coating or combining the said methods. PEEK must be sulfonated in order to be used as PEM material. Sulfonation is a well known process to increase the hydrophilicity and proton conductivity of polymer by attaching sulfonic groups to the polymers' chain. The attached sulfonic groups can offer and retain relatively higher water due to the enhanced antifouling capacity and favorable hydrodynamic environment of the membrane [7], which is also a very important mechanism for proton conducting.

In the current study, a modification of sulfonated PEEK (SPEEK) by blending surface modifying macromolecules (SMM) method is adopted. SMM is a simple blending method which uses the concept of surface segregation in polymer science as detailed elsewhere [8 – 11]. SMM when introduced as an additive in a base polymer will migrate to the surface and change the chemistry of the surface while maintaining its bulk properties. The migration of the hydrophilic or hydrophobic SMM segment is according to the thermodynamic principles of the tendency to minimize the interfacial energy. Due to this fact, when a membrane of blended polymer with SMM is cast, the polymer with the lowest surface energy of hydrophilic or hydrophobic will migrate and concentrate at the top or air interface. The bulk properties remain almost unchanged for a very small amount of SMM, *i.e.* usually less than 5%, is added to the dope solution.

A new formulation of a charged SMM (cSMM) which end capped with sulfonic group was developed, anticipating to increase the hydrophilicity of the blend membrane. It is well documented that the enhancement of hydrophilicity is crucial for a better PEM performance of SPEEK as its proton conductivity is dependent on water uptake [12]. Furthermore, it is expected that the proton conductivity will be further increased by the interaction of the sulfonic group from cSMM with that of SPEEK. Therefore, the objectives of this paper are: to design a novel tailor-made cSMM for blending and modifying SPEEK membranes, to prepare and characterize

such membranes, and to study the said membranes on thermal and mechanical stability.

2.0 METHODS

2.1 Synthesis of Sulfonated Poly(Ether Ether Ketone)

PEEK was sulfonated following the technique described in [13, 14]. A 5 g of PEEK was dried in an oven at 100 °C for 24 hrs and then dissolved in 95 ml of concentrated (95 – 98%) sulfuric acid (H_2SO_4) at room temperature to suppress the heterogeneous sulfonation. After completing the dissolution of PEEK (about 1 h), the polymer solution was brought to the desired temperature of 55°C and held for 3 hrs to obtain the desired degree of sulfonation (DS). In order to terminate the reaction, the polymer solution was poured into excess ice-cold deionized water under continuous stirring for one night to remove the residual acid. The polymer was washed repeatedly with de-ionized water until a neutral pH was reached. Then it was dried in air circulation oven at 60°C overnight. The formation of SPEEK from PEEK is shown in Figure 1. The sulfonated poly(ether ether ketone), SPEEK, is basically a copolymer, consisting of sulfonated PEEK structural unit and original PEEK structural unit.

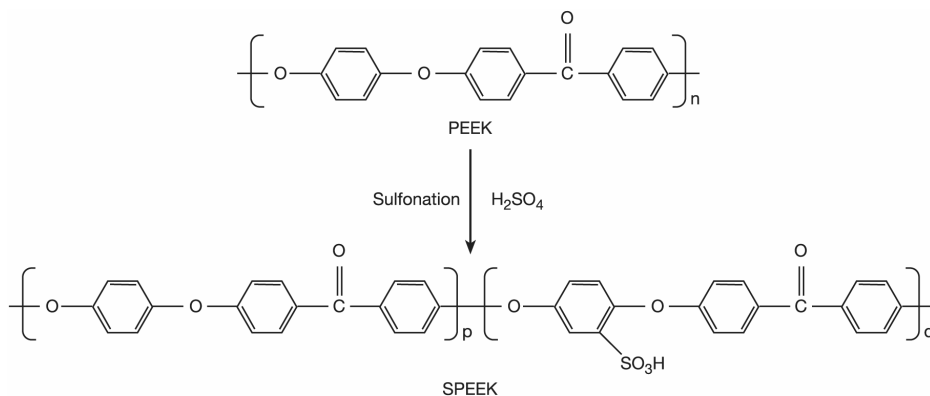


Figure 1 Sulfonation of PEEK

2.2 Characterization of Sulfonated Poly(Ether Ether Ketone)

The characterization of SPEEK was made by measuring the degree of sulfonation (DS) by ^1H NMR (Bruker, USA) at a resonance frequency of 400.13 MHz and at room temperature [14, 15]. The DS is defined as the ratio of the number of the structural units containing sulfonic acid group to the total number of the structural units. The ratio between the peak area of the distinct signal (AH_f) and the integrated peak area of the signals corresponding to all other aromatic hydrogen ($AH_{a,b,c,d,e}$) is expressed as

$$\frac{q}{(12 - 2q)} = \frac{AH_f}{\sum AH_{a,b,c,d,e}} \quad (1)$$

Where q is defined as the ratio (the number sulfonated repeat units/ the number of the intire repeat units) or the degree of sulfonation (DS%) (Figure 1). Equation (1) is valid for $0 < q < 1$.

The ion exchange capacity (IEC) of the membrane was then determined by equation (2) which relates the IEC with DS for SPEEK in hydrogen form.

$$DS\% = \frac{288(IEC)}{1000 - 80(IEC)} \times 100 \quad (2)$$

It should be mentioned that the molecular weight of SPEEK in hydrogen form and PEEK are 368 and 288 respectively. The number (80) arises from the difference between these two molecular weights.

2.3 Synthesis of Charged Surface Modifying Macromolecule

The charged surface modifying macromolecule, cSMM, end-capped with hydroxyl benzene sulfonate, was synthesized using a two-step solution polymerization method. The initial step involved the reaction of methylene bis(phenyl isocyanate) (MDI) with di(ethylene glycol) (DEG) in a common solvent of dimethylacetamide (DMAc). This mixture formed a urethane prepolymer solution. The prepolymer is a segment-blocked urethane oligomer, poly(4,4'-diphenylenemethylene methoxymethylene urethane) having both ends capped with isocyanate. The reaction was then terminated by the addition of Hydroxybenzenesulfonic (HBS) resulting in a solution of charged or sulfonated surface modifying macromolecules (cSMM).

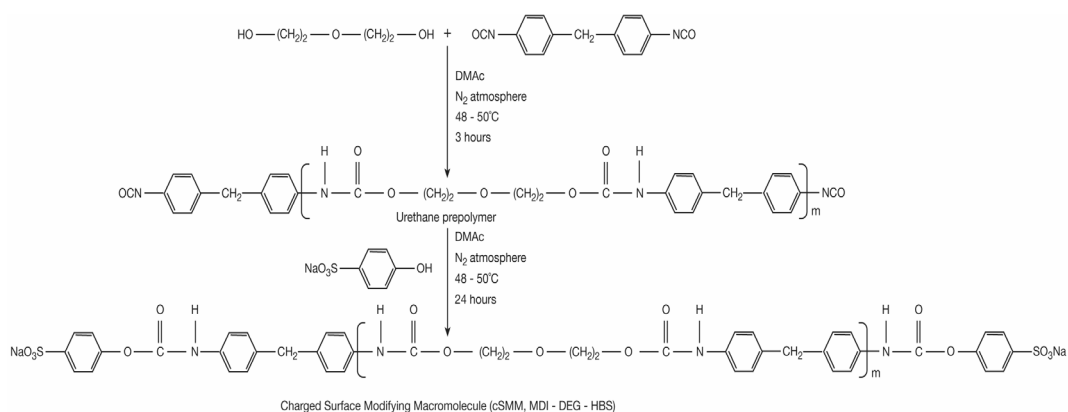


Figure 2 Synthesis of cSMM (MDI-DEG-HBS)

The experimental set-up used for cSMM synthesis is illustrated in Figure 2. The detailed procedures are as follows: to a solution of 0.03 mol (7.5 g) MDI in 50 mL of degassed DMAc was loaded in a 1 L Pyrex round bottom flask. Then, a solution of 0.02 mol (2.122 g) degassed DEG in 100 mL of degassed DMAc was added drop-wise with stirring. The temperature was controlled at 48 – 50 °C. DEG and MDI were allowed to react for 3 hrs. Then 0.02 mol (4.644 g) of HBS dissolved in 50 mL of degassed DMAc was added drop-wise. The solution was left under stirring for 24 hrs at 48 – 50 °C, resulting in a solution of charged surface modifying macromolecules. The scheme of the chemical reaction for the synthesis of cSMM (MDI-DEG-HBS) is shown in Figure 2.

2.4 Characterization of cSMM by FTIR and Elemental Analysis

The existence of sulfonic group in the cSMM polymer can be confirmed by FTIR. Characteristic bands of the aromatic sulfonate salt. The FTIR is also used to confirm the existence of the sulfonic group in the SPEEK membrane as well as the SPEEK/cSMM blend membrane.

2.5 Preparation of Membranes

Ten gram of SPEEK was dissolved in 90 g 1-Methyl-2-pyrrolidinone (NMP) to make a 10 wt% of original SPEEK solution. The blend solutions were prepared by mixing 0.416 g of each cSMMs and 10 g of SPEEK, to make 4 wt% of cSMM in total solid. Both mixtures were stirred for 24 hrs, before the mixtures were cast onto a glass plate using a pneumatic casting machine. The membrane was dried at 120 °C for 24 hrs in a vacuum oven. After cooling to room temperature, the membrane was peeled off from the glass in de-ionized water. Finally, the membrane was converted into the H⁺ form by immersing it into a 1 M sulfuric acid solution for 24 hrs at the room temperature and blotted dry with absorbent paper before it was air dried.

2.6 Characterization of Membrane

2.6.1 Contact Angle Measurements

The contact angle, CA, of the membrane surface was measured using a VCA Optima Surface Analysis System (AST Products, Inc., Billerica, MA). Sample coupons with an area of about 5 cm × 1.5 cm were prepared by cutting pieces at random locations within the membrane sheet. The sample was placed on a glass plate and fixed with a tape. Then, a drop of distilled water (2 µL) was placed on the sample surface using a micro syringe (Hamilton Company, Reno, NV). The CA was measured within a 30 sec period after the water drop was placed. The CAs were measured at ten different spots on each membrane sample coupon and the values are averaged.

2.6.2 Water Uptake Measurement

The membrane was dried in an oven at 60 °C for 48 hrs, weighed, soaked in de-ionized water overnight at room temperature, blotted dry with absorbent paper to remove any surface moisture, and re-weighed. Then, % of water uptake was calculated from the equation below,

$$\text{Water uptake\%} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (3)$$

where W_{wet} and W_{dry} are the weight of the wet and the dry membrane respectively. The accuracy of the measurement is within $\pm 7\%$.

2.6.3 Fourier Transforms Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy was used to observe the presence of sulfonic acid groups in cSMM and SPEEK as well as the interactions between SPEEK and cSMM in the blended membrane. The FTIR spectrometer (Magna-IR 560, Nicolet, Madison, MI, USA) equipped with attenuated total reflection (ATR) having a germanium (Ge) spherical crystal. The spectra were measured in absorbance mode over a wave number range of 2000 to 700 cm^{-1} .

2.6.4 Scanning Electron Microscopy

The morphology of the blend membrane was investigated using scanning electron microscopy (SEM). Specimen for the SEM was prepared by freezing the dry membrane sample in liquid nitrogen up to 3 min and breaking it to produce a cross-section. Fresh cross-sectional cryogenic fractures of the membrane was vacuum sputtered with a thin layer of gold by using an ion sputtering (Biorad Polaron Division, Hertfordshire, UK) before viewing on the scanning electron microscope (SEMEDAX; XL 40; PW6822/10, Phillips, UK) with a potential of 10 kV.

2.6.5 Thermal Stability Studies

The glass transition temperature (T_g) was examined by differential scanning calorimeter (DSC) equipped with universal analysis 2000 program (DSC Q1000-0760, TA Instruments, New Castle, DE). Indium was used for the calibration of the temperature. About 10 mg of polymer was crimped into aluminum pan. The polymers were annealed at about +50 °C for 10 min under nitrogen atmosphere and then quenched, and scanned at a heating rate of 10 °C min^{-1} . The sample weight loss was measured by thermogravimetric analysis (TGA) using thermogravimetric analyzer (Mettler, Toledo, OH). A pre-oven dried sample of 10 mg was heated under room temperature to 800 °C at the heating rate 10 °C min^{-1} in air.

2.6.6 Mechanical Strength Study

The tensile strength of the membrane was measured using mechanical testing system, MTS (LRX 5kN, Lloyd Instruments, Fareham, Hants, UK). The gauge length and width of dumbbell tensile specimens were 15 and 4 mm respectively. The specimen was placed between the grips of the testing machine, and the speed of testing was set at the rate of 5 mm min⁻¹. Five specimens were taken from each type of membrane for the measurement and their average value was calculated. The accuracy of the measurement is within $\pm 5\%$.

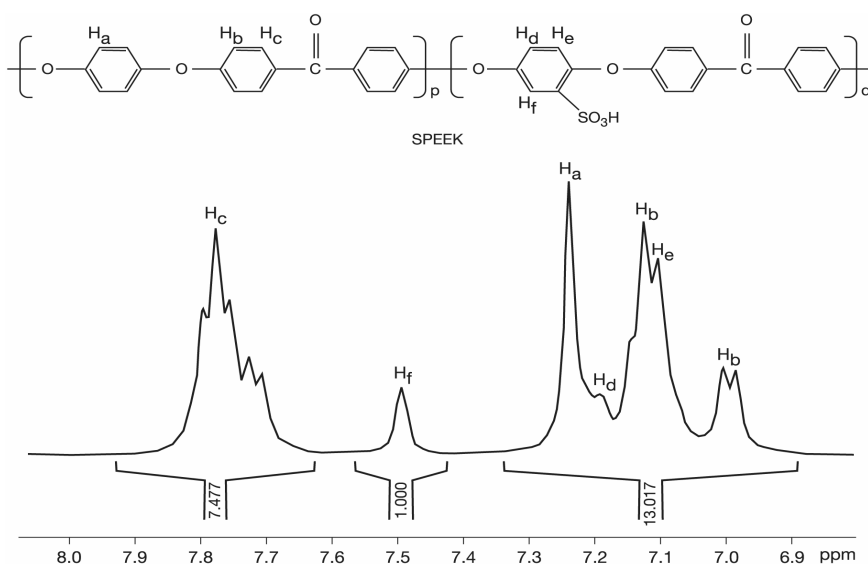


Figure 3 ^1H NMR spectrum of SPEEK

3.0 RESULTS AND DISCUSSION

3.1 Polymer Characterization

Degree of sulfonation of SPEEK was determined using ^1H NMR analysis from equation (1) as shown in Figure 3, and was found to be 53.35 DS%. The H_f signal is equivalent to the sulfonic acid group content and the other peak signals represent the rest of the hydrogen existing in the SPEEK repeat unit. By using the DS value from ^1H NMR analysis, its IEC value was calculated from equation (2) to be 1.613 meq/g.

The existence of sulfonic group in the cSMM polymer can be confirmed by FTIR as shown in Figure 5. Characteristic bands of the aromatic sulfonate salt are observed at 1224, 1069 and 1018 cm^{-1} . The figure proved that the newly synthesized cSMM contains sulfonic group.

3.2 Membrane Characterization

Mixing SPEEK and cSMM in NMP formed homogeneous and transparent solution however, after casting on a glass plate the blended membrane was more yellowish than the original SPEEK. Mixing cSMM into SPEEK, due to the similar chemical structure of sulfonic group, is first miscible but then cSMM are expected to migrate upwards to the membrane surface. Therefore, the cSMM has dispersed homogeneously into SPEEK. The homogeneity of dispersions of cSMM in SPEEK was examined with SEM.

Figure 4 shows the SEM pictures of high magnification. In both, nodular structures are observed. Judging from the size of each spherical unit, it represents the super nodular aggregates. There is a notable increase in the size of the sphere from the SPEEK to the SPEEK/cSMM blend membrane suggesting an increase in free volume that can be associated with the intake of water molecules.

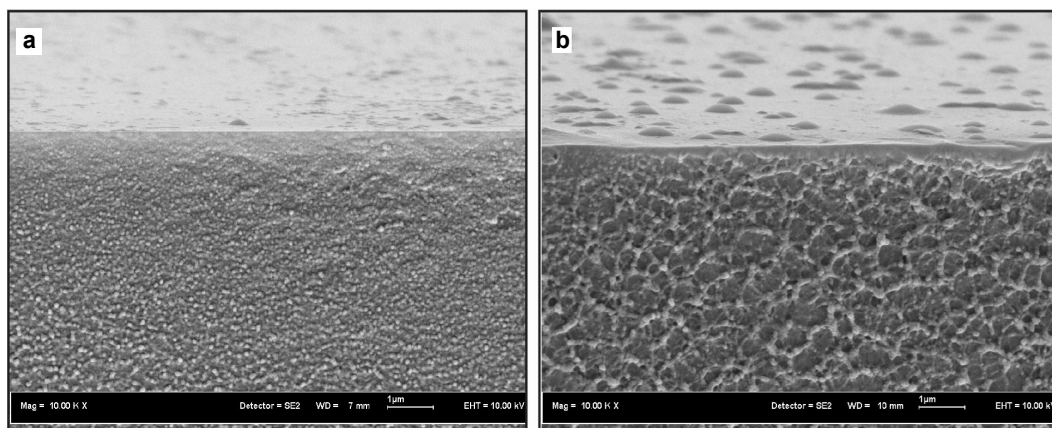


Figure 4 SEM picture of crosssectional area of (a) original SPEEK and (b) SPEEK/cSMM

The SPEEK and SPEEK/cSMM membrane were also analyzed by FTIR. The purpose of FTIR spectroscopy test is to examine the presence of sulfonic group in the membrane samples. The FTIR spectra of SPEEK and SPEEK/cSMM blend membrane are shown in Figure 5, which is to confirm the presence of sulfonic group in both membranes. The presence of sulfonic group in SPEEK and SPEEK/cSMM blend membrane can be confirmed by the absorption bands at 1222.7 (asymmetric O=S=O), 1081 (symmetric O=S=O), 1024 (S=O). FTIR spectra of both membranes were nearly identical. However, by calculating the height of each peak, as presented in Table 1, there is a difference in height at the three particular peaks. This indicates that by adding the cSMM the intensity of the sulfonic group has increased as compared to the original SPEEK. This is most probably due to the extra sulfonic group on the top surface of the blend membrane.

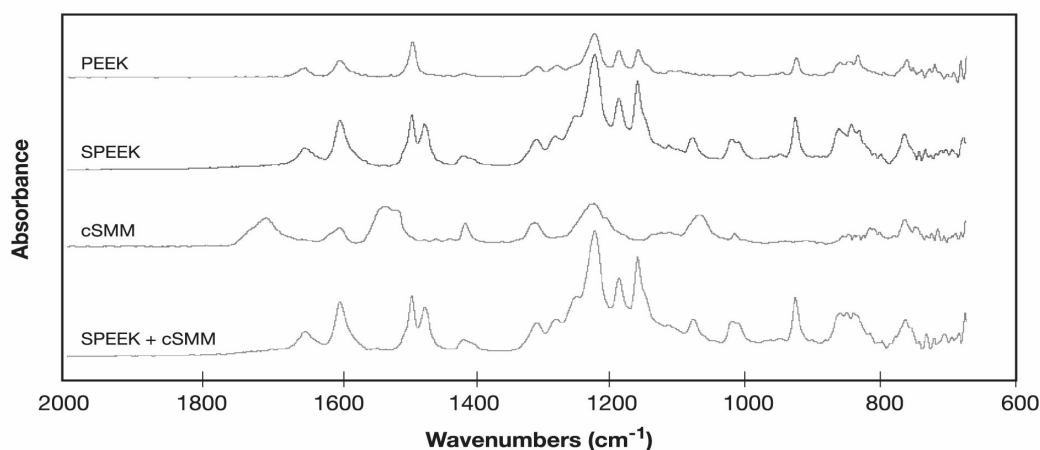


Figure 5 FTIR spectra of polymer and membrane in the study

Table 1 The height of $-\text{SO}_3\text{H}$ identity peak in membrane

Peak height Membrane	Peak 1222.7	Peak 1081	Peak 1024
SPEEK	0.0566	0.0164	0.0259
SPEEK/cSMM	0.075	0.022	0.031

The hydrophilicity of the membrane surface can be evaluated by measuring the contact angle (CA). Table 2 shows the results of the CA measurement. SPEEK is significantly higher than SPEEK/cSMM blend at the top surface. The CA of SPEEK was also higher than SPEEK/cSMM blend at the bottom surface. Comparing the top and the bottom surface, the difference is not significant for SPEEK, while the CA of the top surface was significantly lower than the bottom surface for SPEEK/cSMM blend. This is most likely due to the migration of cSMM to the top surface, covering the surface with the sulfonic end groups that are protruded vertical to the surface while the urethane prepolymer part of cSMM is anchored to the host SPEEK.

Table 2 Characterization of Nafion 112, SPEEK, and SPEEK/cSMM films

Polymer film	Water uptake (%)	CA ($^{\circ}$) Top-surface	CA ($^{\circ}$) Bottom-surface	T _g ($^{\circ}\text{C}$)	Tensile strength (MPa)
Nafion 112	20	80	80	143.6	34.8
SPEEK	32	83.12 \pm 2.36	84.64 \pm 3.07	151.5, 215.4	45
SPEEK/cSMM	38	65.82 \pm 2.97	79.47 \pm 2.80	210.27	39

Table 2 also shows that water uptake increased significantly from SPEEK to SPEEK/cSMM blend. The result shows the total water content of SPEEK is 32% and the total water content of the blend membrane increased to 38% due to the increased hydrophilicity from the cSMM. This is further supported by the increase in nodule size and free volume that can be associated with the intake of extra water molecules, as discussed above.

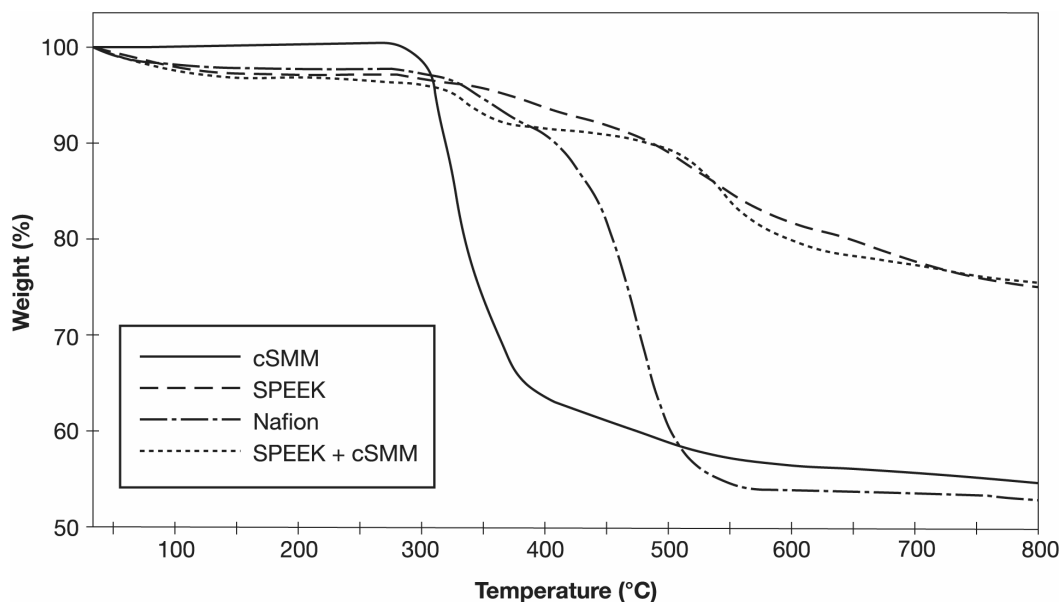


Figure 6 Thermal decomposition curve of polymer and membrane in the study

3.3 Thermal Stability

Thermal stability of Nafion112, SPEEK, SPEEK/cSMM blend as well as cSMM was determined by TGA. Figure 6 shows the TGA thermograms. Regarding cSMM, weight decrease of about 5% was observed as the temperature was raised to 300 °C, followed by a steep decrease in weight of another 75% when the temperature was raised from 300 °C to 550 °C. This is due to the removal of sulfonic groups [21] and the decomposition of the polymer chain of polyurethane backbone occurring simultaneously. Compared to cSMM, SPEEK seems far more stable. Since the cSMM is a minor component (4%) of the polymer blend, its effect on the thermal stability seems only marginal. As for the blend membrane, the decomposition was found to be greater between temperature of 300 °C to 400 °C as compared to pristine SPEEK. This is due to the decomposition of sulfonic group in the membrane. This result revealed that the blend membrane contains more sulfonic group than the SPEEK.

The T_g of polymer samples are also shown in Table 2. According to the result, T_g for SPEEK were detected at 215.4 °C. The T_g of cSMM and SPEEK/cSMM blend are 114.6 °C and 210.3 °C, respectively. About 2.4% reduction in T_g of the blend is most probably because of the presence of cSMM has reduced the rigidity of the SPEEK structure.

3.4 Mechanical Stability

The results of the tensile strength measurement are presented in Table 2. From the table, the tensile strength of SPEEK is 45 MPa similar to the reported value by [1], while the tensile strength of SPEEK/cSMM blend is 39 MPa. Thus, the incorporation of cSMM in SPEEK has reduced the tensile strength by 14%. This is due to the reduction in the rigidity of the polymer. The tensile strength of SPEEK/cSMM is however still higher than that of Nafion 112.

From the findings, cSMM is clearly a good candidate as an additive for SPEEK in improving its function as polymer electrolyte membrane. The addition of cSMM with an additional SO_3^- charge has enabled the water uptake to be increased which is crucial to enhance the proton conductivity that of SPEEK.

4.0 CONCLUSION

The following conclusions can be drawn from the experimental results.

- (1) The newly synthesized cSMM indeed carries charged sulfonic groups.
- (2) Surface migration of cSMM occurs when blended into SPEEK membrane.
- (3) Blending cSMM into the SPEEK membrane decreases T_g and tensile strength.
- (4) The SPEEK/cSMM blend membrane absorbs more water as compared to the pristine SPEEK.
- (5) cSMM is a potential material to be blended into SPEEK membrane in order to increase its PEM performance.

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